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PHOSPHORUS SORPTION KINETIC ON ACID UPLAND SMECTITIC SOIL AMENDED WITH CALCIUM CARBONATE AND CALCIUM SILICATE

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ABSTRACT

Acid upland smectitic soil is identified by high amount of exchangeable Al due to the weathering of aluminum (Al) octahedral layer by H^+ saturation and by very low phosphorus (P) status. Calcium carbonate ($CaCO_3$) and calcium silicate ($CaSiO_3$) were commonly used to decrease exchangeable Al and increase soil pH. Laboratory experiments were conducted with clayey smectitic Typic Paleudults from Gajrug region, West Java. The $CaCO_3$ and $CaSiO_3$ were added at rates to replace 0, 1.5 or 3 times of exchangeable Al. After one month of incubation, P sorption kinetic experiments were conducted. The changes in some chemical properties after one month incubation showed that both $CaCO_3$ and $CaSiO_3$ increased the soil pH, exchangeable Ca, and base saturation but did not increase the cation exchange capacity. The results of the experiment showed that both $CaCO_3$ and $CaSiO_3$ decreased the rate constant value of first order kinetic equation (k) and the P sorbed maximum (a) at given amount of added P compared to Control. The $CaCO_3$ was better than $CaSiO_3$ in decreasing k values and on the contrary for a values. The decrease in P maximum sorption and the rate constant of the soil amended with $CaSiO_3$ and $CaCO_3$ due to occupation of P sorption sites by silicates and hydroxyl ions. The $CaCO_3$ with the rate to replace 1.5 x exchangeable Al was recommended to decrease the rate constant of P sorption. However, the $CaSiO_3$ at the rate to replace 3 x exchangeable Al was recommended to decrease the maximum P sorption.

Key words: Acid Smectitic Soil, Lime, P- sorption Kinetic, Silicate

INTRODUCTION

Acid upland smectitic soils in tropical region are generally high in exchangeable aluminum (Al), deficient in phosphorus (P) and sorb large quantity of this element. Liming using calcium carbonate ($CaCO_3$) and calcium silicate ($CaSiO_3$) is frequently used to raise soil pH and increase phosphorus bioavailability (Sanchez and Uehara, 1980). However the use of liming materials are controversial concerning P sorption experiments. Several authors reported that liming decreases P sorption (Smyth and Sanchez, 1980; Haynes, 1982; Anjos and Rowel, 1987; Naidu *et al*., 1990; Hartono, 2008). Other studies reported that liming increase P sorption (Chen and Barber, 1990) and others have shown no significant influence (Arias and Fernandez, 2001).

The decrease in P sorption caused by liming were reported due to the increase in hydroxyl ion concentration. The increase in hydroxyl ion concentration increased competition between hydroxyl and P for specific adsorption site on mineral surface (Anjos and Rowel, 1987; Smyth and Sanchez, 1980). Other scientific reason was that hydroxyl ion reacts with aluminum (Al) ion and hydroxyl-Al ion forming Al-hydroxides therefore decreasing the number of P sorption sites (Naidu *et al*., 1990). Furthermore Haynes (1982) explained that the mineral surface became increasingly negative with increasing pH resulting in greater electrostatic repulsion and decreased P sorption.

Concerning the pH, Chen and Barber (1990) reported that when the pH of acid weathered soils were uplifted from pH 4.2 to pH 8.3 increased sorbed P up to pH of about 6.0. However at pH higher than 6.0 decreased P sorption. The initial increase in P sorption was explained due to formation of amorphous hydroxyl Al with highly active sorbing surfaces. The decrease in P sorption at pH higher than 6.0 was attributed to increased competition of hydroxyl with phosphate for sorption sites.

Few studies have focused on P sorption kinetic on acid upland smectitic soils. The exchangeable Al of these soil are very high due to the weathering of Al octahedral layers by H^+. These soils also have very low soil P status. Phosporus management is very important concerning uplifting the soil fertility. Liming is one of the management to uplift soil fertility. Materials for liming are usually $CaCO_3$ and $CaSiO_3$.

The objective of this study was to evaluate the P sorption kinetic in acid upland smectitic soil amended with $CaCO_3$ and $CaSiO_3$.

MATERIALS AND METHODS

Soil samples. Soil samples of surface horizon of cultivated clayey smectitic Typic Paleudult from Gajrug West Java were collected. The coordinates of sampling site were S 06^O 30' 43.3" and E 106^O 22' 49.4" with an elevation of 210 m above sea level. Soil samples were air-dried and crushed to pass through a 2-mm mesh sieve.

Methods of initial soil analyses. Soil pH was measured in a 1:1.5 (w/v) water solution using a pH meter. Clay content was determined with pipet method. Clay minerals were identified by X-ray diffraction analysis (Rigaku RAD-2RS Diffractometer). The content of organic carbon (C) in soil was measured with a NC Analyzer (Sumigraph NC analyzer NC-800-13 N, Sumika Chem. Anal. Service). Available P content was obtained

by the Bray 1 method (Bray and Kurtz, 1945) while total P was determined by digesting the soil sample using concentrated percloric acid and nitric acid as described by Kuo (1996). Their absorbance at 693 nm was determined using a UV-VIS Spectrophotometer (UV-1200, Shimadzu Corporation, Japan). Cation Exchange Capacity (CEC) was obtained by extraction with 1 mol L^{-1} NH_4OAc pH 7.0 and the contents of exchangeable bases calcium (Exch. Ca) and magnesium (Exch. Mg) were determined by Atomic Absorption Spectrophotometry (AA-640-12, Shimadzu Corporation, Japan) while those of exchangeable potassium and sodium were determined by flame emission spectrophotometry (AA-640-12, Shimadzu Corporation, Japan). Base saturation was defined as the ratio of total exchangeable bases to CEC, expressed as a percentage. Exchangeable Aluminum (Al) was extracted with 1 mol L^{-1} KCl.

The contents of oxalate-extractable Fe and Al (Fe_o and Al_o) were obtained by extraction with 0.3 mol L^{-1} ammonium oxalate, at pH 3 for 4 hours in a dark room (McKeague and Day, 1966). Extracted Fe and Al of Al_o and Fe_o were filtered through a syringe filter with a 0.45 µm pore size (Minisart RC 15, sartorius, Hannover, Germany). Contents of extracted Fe and Al were then determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (SPS1500, SEIKO).

Incubation experiment. 300 g (oven-dry weight) soil was put into a plastic pot and incubated with $CaSiO_3$ or $CaCO_3$ where both of them were grade laboratory for one month. A completely randomized design in double replication was set up. The experiment consisted of 3 levels of calcium silicate or $CaCO_3$ to replace 0, 1.5 or 3 x exchangeable Al. Deionized water was added to the pots to maintain the soil moisture around 85 % of field capacity every second day gravimetrically. After the period of incubation, the soil samples were air-dried.

Phosporus a sorption kinetic experiment. Duplicates of 3 g samples (< 2 mm) were equilibrated in 30 mL of 0.01 mol L^{-1} $CaCl_2$ containing 50 mg P L^{-1} as KH_2PO_4. Two drops of toluene were added to suppress the microbial activity. The suspension was shaken for 1 minute (mint), 5 mint, 10 mint, 15 mint, 20 mint, 30 mint, 1 hour (h), 3 h, 6 h and 48 h. As in P sorption experiment, in the end of the shaking period, the soil suspensions were centrifuged at 2500 rpm for 15 minutes and filtered (filter paper No. 6, Advantec Toyo, Tokyo, Japan). Phosporus content in the supernatant solution was determined by the procedure of Murphy and Riley (1962). The absorbance at 693 nm was determined using a UV-VIS spectrophotometer (UV-1200, Shimadzu Corporation, Japan). The amount of P sorbed by the soils was calculated as the difference between the amount of P added and the amount remaining in solution. Phosporus sorption kinetic experiments were conducted at 25° C.

For describing the P sorption kinetic, the data was fitted to first order kinetic equation as below.

P sorbed = $a\ (1\text{-}e^{-kt})$

where the constant a is the P sorbed maximum at given amount of P added in mg kg^{-1}, k in h^{-1} is the rate constant of P sorption and t in h is shaking period.

Statistical analyses. Analyses of variance followed by a Tukey's test were applied to evaluate the effect of calcium silicate to the parameters. SYSTAT 8.0 was used for the statistic analyses (SPSS Inc. 1998).

RESULTS AND DISCUSSION

Physicochemcal Properties of Soil

The physicochemical properties of the Gajrug soil are presented in Table 1. The values were judged using criteria published by Soepratohardjo (1983). Soil was very acid with very high exchangeable Al. The value of the exchangeable Al was very high (24.4 $cmol_c$ kg^{-1}) compared to the others acid upland soils. This was because of the replacement of Al in the octahedral with H^+ of clay minerals smectite. This replacement resulted in high exchangeable Al. The clay mineral analyses of the Gajrug soil is presented in Figure 1. Figure 1 showed that its characteristics XRD pattern was smectite. Smectite had very short time for Al replacement with H^+ (Bohn *et al*., 1985). The Cation Exchange Capacity (CEC) of the Gajrug soil was vey high. It is understandable that gajrug soil had high clay content (65 %) with smectite in its clay minerals. CEC was very related to clay content and kind of clay minerals (Hartono *et al*., 2005).

The available P (Bray-1 P) and total-) were low. The available P was about 5.65 mg kg^{-1} and the total-P was 375 mg kg^{-1}. The low P contents were due to low application of P fertilizer. The Ca content was low while Mg and K contents were medium. The base saturation of this soil was very low. C-organic and N-total were medium.

Judging from the exchangeable Al and P content of this soil, efforts concerning to find suitable amendment to decrease exchangeable Al and uplift in the P contents were necessary.

The Change in Some Selected Chemical Properties of the Soil after Incubation

The changes in pH, exchangeable Al, CEC, bases (Ca, Mg, K and Na) and base saturation are presented in Table 2. Soil pH increased two to three unit reaching the neutral point after incubation by $CaCO_3$ and $CaSiO_3$. All rates of $CaCO_3$ and $CaSiO_3$ decreased exchangeable Al.

Table 1. Physicochemical properties of the soil sample.

Physicochemical properties	value	status
pH H_2O (1:1.5)	4.24	very acid
pH KCl (1:1.5)	3.80	-
Organic C (%)	2.52	medium
N-total (%)	0.22	medium
Clay content (%)	70.0	-
CEC ($cmol_c\ kg^{-1}$)	40.3	very high
Ca^{2+} ($cmol_c\ kg^{-1}$)	4.29	low
Mg^{2+} ($cmol_c\ kg^{-1}$)	1.05	medium
K^+ ($cmol_c\ kg^{-1}$)	0.51	medium
Na^+ ($cmol_c\ kg^{-1}$)	0.18	low
Base saturation (%)	15.0	Very low
Exchangeable Al ($cmol\ kg^{-1}$)	24.4	-
Al saturation (%)	80.2	very high
Bray-1 P ($mg\ kg^{-1}$)	5.65	low
Total-P ($mg\ kg^{-1}$)	375	low
Phyrophosphate:		
Al (Al_p)	4.97	-
Fe (Fe_p)	4.15	-
Oxalate:		
Al (Al_o)	6.38	-
Fe (Fe_o)	9.11	-
Dithionite-Citrate-Bicarbonate (DCB):		
Al (Al_d)	8.67	-
Fe (Fe_d)	29.2	-
Clay (%)	65.0	

Tabel 2. Some chemical properties after one month incubation.

	pH H_2O	Exch. Al	CEC
		.....$cmol_c\ kg^{-1}$.....	
Without treatment	4.73a	24.7	40.3a
$CaCO_3$ level 1.5	6.38b	nd	38.6a
$CaCO_3$ level 3	7.69c	nd	39.8a
$CaSiO_3$ level 1.5	5.82b	nd	40.4a
$CaSiO_3$ level 3	7.60c	nd	43.8a

Nd: not detectable

The CEC was not affected because the negative charges in soil was from isomorphic substitution. As shown in Figure 1, only smectite was the soil clay mineral. The negative charge of smectite was from isomorphic substitution so the changes in pH even to neutral point did not affect the CEC values. From the changes of some selected chemical properties, the application of $CaCO_3$ or $CaSiO_3$ to replace 1.5 x exchangeable Al were sufficient to improve those chemical properties.

Phosporus Sorption Kinetic Parameters

The amount of P sorbed by the soil samples in relation to shaking period is presented in Table 3 and in Figure 2. The data were simulated and fitted to first order kinetic equation. The parameters of first order kinetic equation are presented in Table 4. The parameters of *k* and *a* are the rate constant of P sorption and P sorbed maximum at given amount of added P respectively.

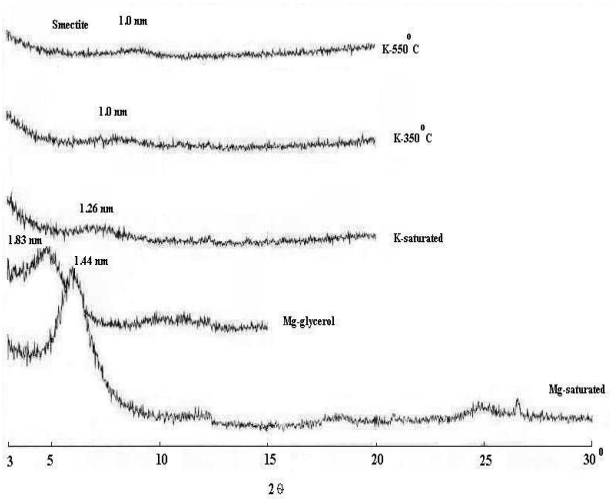

Figure 1. Identification of Smectite using its characteristic XRD pattern of soil samples.

Table 3. Phosporus sorbed with Shaking period.

	Shaking Period									
	0.02 h	0.08 h	0.17 h	0.25 h	0.33 h	0.50 h mnt	1 h	3 h	6 h	48 h
Treatment	P sorbed (mg kg^{-1})									
Without treatment	552	551	556	560	555	558	562	565	566	567
$CaCO_3$ level 1.5	506	513	525	556	537	543	553	560	562	565
$CaCO_3$ level 3	512	524	532	554	542	548	555	561	562	565
$CaSiO_3$ level 1.5	518	500	498	543	518	531	544	549	556	563
$CaSiO_3$ level 3	481	451	452	503	475	495	514	532	533	552

h : hour

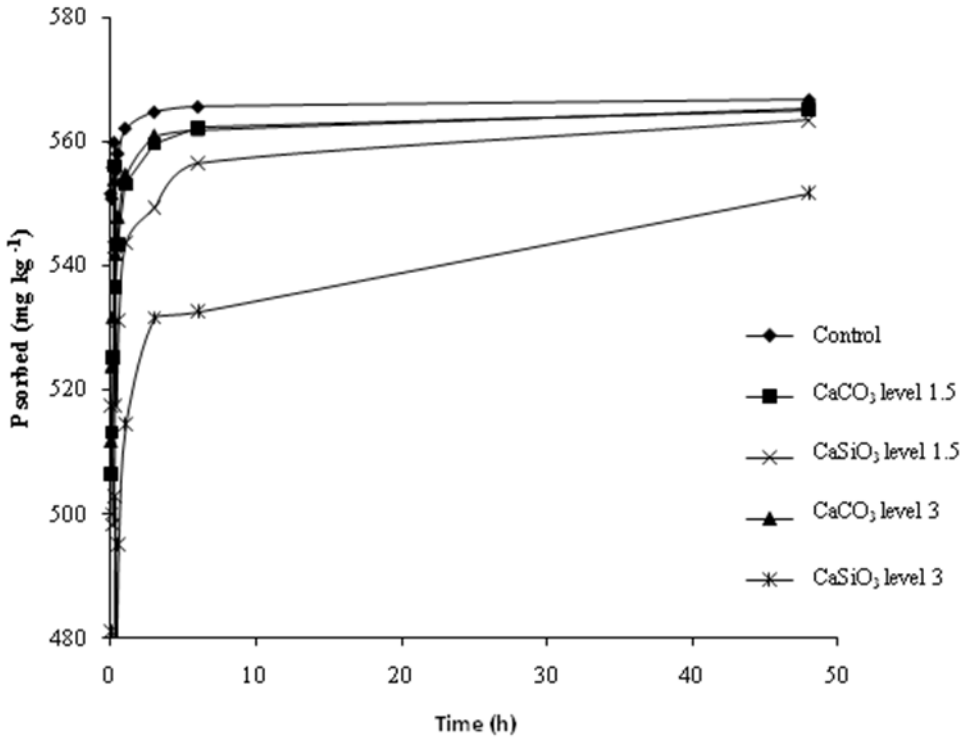

Figure 2. Phosporus sorption kinetic by soil samples at 25 ^{o} C

As shown in Table 3 and Figure 2 P sorption was very fast. The added P in this P sorption kinetic experiment was 50 mg P L^{-1} or equivalent with 579 mg P kg^{-1}. For sample without liming, in one minute, about 95 % of added P was sorbed. In one minute in soil samples treated with $CaCO_3$, P sorbed were decreased to 88 % and 89 % by rate of $CaCO_3$ to replace 1.5 x exchangeable Al and 3 x exchangeable Al respectively. Meanwhile in soil samples treated with $CaSiO_3$, P sorbed were decreased to 89 % and 83 % by rate of $CaSiO_3$ to replace 1.5 x exchangeable Al and 3 x exchangeable respectively. Application of $CaSiO_3$ to replace 3 x exchangeable Al was more promising to decrease the amount of P sorbed by the soil. The lower P sorbed values on the samples treated by calcium silicate with the rate to replace 3 x exchangeable Al constantly showed in each shaking period.

The *k* value which refers to the rate constant of sorption of soil sample treated by $CaCO_3$ and $CaSiO_3$ was statistically significantly lower than that of control (Table 4). As for comparison between $CaCO_3$ and $CaSiO_3$, $CaCO_3$ decreased the *k* values of P sorption lower than those of $CaSiO_3$. The rate of $CaCO_3$ to replace 1.5 exchangeable Al was lower significantly than those of $CaSiO_3$.

Table 4. The parameters of the equation of the first order kinetic.

Treatment	*k*	*a*	R^2 value of the equation
	h^{-1}	(mg P kg^{-1})	
Without treatment	4.17a	567a	0.99
$CaCO_3$ level 1.5	2.60b	566b	0.99
$CaCO_3$ level 3	2.70bc	566c	0.99
$CaSiO_3$ level 1.5	3.49d	562d	0.98
$CaSiO_3$ level 3	3.20e	550e	0.96

Means followed by the same letter within a column are not significantly different (Tukey`s test, $P < 0.05$)

Concerning the *a* values which refers to the P sorbed maximum, both $CaCO_3$ and $CaSiO_3$ decreased the value significantly. However, the increasing rates of $CaSiO_3$ decreased the *a* value lower than those of $CaCO_3$.

From the P sorption kinetic experiment, it is suggested that silicate and hydroxyl ions occupied the sorption sites competing with P ions. Hydroxyl ions were from reaction between silicate ions and hydrogen ions

forming weak silicate acid. This reaction was indicated by increase in soil pH. As the results, the P sorbed maximum of the soil was decreased and also the rate constant of P sorption. As for treatment with $CaCO_3$, reaction between bicarbonate ions and hydrogen ions forming weak carbonate acid contributed to the increase of hydroxil ions. These hydroxyl ions competed with P to the sorption sites (Anjos and Rowel, 1987; Smyth and Sanchez, 1980). The possibility that the decreased P sorbed maximum and rate constant of P sorption because of the increase in negative charges due to increased pH was not supported by the obtained CEC data. CEC did not increase with the increasing rates of $CaCO_3$.

CONCLUSION

Application of $CaSiO_3$ and $CaCO_3$ decreased P sorbed maximum and the rate constant of the smectitic soil contanining high exchangeable Al. The decrease in P sorbed maximum and the rate constant of the soil amended with $CaSiO_3$ and $CaCO_3$ were due to occupation of P sorption sites by silicates and hydroxyl ions.

$CaCO_3$ with the rate to replace 1.5 x exchangeable Al was recommended to decrease the rate constant of P sorption. However, $CaSiO_3$ with the rate to replace 3 x exchangeable Al was recommended to decrease the P sortion maxima.

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